RESEARCH PAPER

EFFECT OF WASTE PLASTICS ADDITION ON THE REDUCTION OF IRON OXIDE BY METALLURGICAL COKE

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ABSTRACT

This work investigates the effect of waste plastics (high density polyethylene (HDPE)) addition on the production of premium grade iron nuggets from iron oxide using metallurgical coke as reducing agent. Composite pellets were formed from mixtures of iron oxide and carbonaceous materials consisting of coke, HDPE and three blends of coke-HDPE. The iron oxide-carbonaceous material composites were heated very rapidly in a laboratory scale horizontal tube furnace at 1500°C in a continuous stream of argon and the off gas was analysed continuously using an online infrared gas analyser and a gas chromatographic analyser. Elemental analyses of samples of the reduced metal were performed chemically for its carbon content and the extent of reduction was calculated based on a mass balance for removable oxygen. The results indicate that blending of coke with HDPE has the beneficial effect of improving the extent of reduction of iron oxide, with the time for complete reduction improving significantly from 600s (Coke) to 330s for Blends 1 and 2. Blending of coke with HDPE led to over 20% reduction in direct carbon dioxide emissions.

Keywords: *HDPE, coke, reduction, carburisation, iron oxide*

INTRODUCTION

In the last few years the demand for high quality scrap steel has soared almost to the point of being scarce in most steel producing countries. This situation (exacerbated by the increasing popularity of electric arc furnaces (EAF) along with the emergence of ultra-high productivity (UHP) furnaces calls for alternative iron materials (AI), as substitute for scrap.

Current and emerging technologies (e.g. HIQIP, FASTMET, ITmk3, etc.) utilised in the production of AIs are based on natural gas or low quality coals as reductants for iron oxide reduction (Sawa *et al.*, 2001).While it is impossible to expand gas-based AI processes due to limited and localised supply of natural gas, the reduced iron in the coal-based processes con-

tains a relatively high slag content from coal ash and gangue, which results in increased lime addition and electrode consumption (Sawa *et al.*, 2001). Besides, some steel producing countries have limited or no sources of coal or natural gas, necessitating the need for the development of novel processes based on local energy conditions and raw materials.

Ghana has three main iron ore deposits of potential industrial and commercial importance, namely the Shieni sedimentary, Opon–Mansi lateritic and the Pudotitaniferous-magnetiferous deposits from which these AIs could be produced directly to feed its existing steelmaking industries.

One potential group of materials that could wholly or partially replace coal and/or natural gas is postconsumer plastics. The generation of this category of waste stream has increased tremendously in recent years because the annual consumption rate of plastic materials has seen a consistent increase from around 5 million tonnes in the 1950's to nearly 100 million tonnes by 2005 (Recycling Survey, 2005).

The use of waste polymeric materials as chemical feedstock in iron and steelmaking has not been widely investigated. Moreover, most of the research on the reduction of iron oxides has focused on the use of carbon (in the form of graphite or metallurgical coke) as a reducing agent. Polymers like polyethylene contain both carbon and hydrogen and their thermal decomposition at high temperatures generates significant amounts of methane and hydrogen, which are known reductants of metal oxides (Nishioka *et al.*, 2007; Dankwah *et al., 2012,* Dankwah *et al., 2014;* Dankwa and Koshy*, 2013,* Dankwa and Koshy, 2014).

In the present work, the potential for producing carburised nuggets of metallic iron from hematite using HDPE and its blends with coke as reducing and carburising agents is investigated under inert atmosphere in a custom made horizontal tube furnace. Discussions on the effect of HDPE addition on the extent of reduction, carburisation and gas emissions are highlighted as well.

MATERIALS AND METHODS
Materials and preparation
Metallurgical coke (obtained from One Steel Sydney Mill, Australia) and its blends with granulated HDPE (obtained from Qenos Pty. Ltd., Victoria, Australia) were employed in this study as carbonaceous materials (Table. 1). The chemical composition (wt %) of the samples and the ash analysis are given in Tables 2- 3. Pulverised reagent grade iron oxide assaying 96.89% Fe_2O_3 was obtained from Ajax Fine Chem Pty Ltd, Taren Point, NSW, Australia; its composition was determined by XRF analysis and the result is given in Table 4. Samples of coke were ground and sieved to particle size in the range of -470 +450µm while samples of granulated HDPE were crushed to smaller sizes by using a cutting mill "Pulverisette 15" (Fritsch GmbH, Idar-Oberstein, Germany). By means of a sieve insert with 0.5mm trapezoidal perforations in the cutting mill, a particle size -470 +450µm, similar to that of coke was obtained. Blends of coke/HDPE were prepared in three different proportions and along with raw coke and raw HDPE, five reductants were utilised for this investigation. Fixed masses of iron oxide (~ 1.86g) were subsequently mixed with the carbonaceous reductants (~ 30 wt. %) and compacted in a die to produce cylindrical pellets (~ 14mm thick and 15mm diameter) by applying a load of 7.5 tonnes for 120s in a hydraulic press.

Methods
Thermal decomposition studies
The hydrocarbonaceous materials (HDPE and coke-HDPE) were mixed thoroughly with alumina powder(-150µm) and cylindrical pellets were formed from the resulting mixture by applying a load of 7.5 tonnes for 60s in a hydraulic press. The use of alumina powder was to slow down the decomposition process (to enable gas measurements by the IR analyser) as well as mimic the reduction environment through the cylindrical pellets. The alumina

Table 1: Blend compositions of the different carbonaceous materials utilised in this study

Carbonaceous material	Coke	Blend 1	Blend 2	Blend 3	HDPE
Coke (wt %)	100	90	80	70	0
HDPE (wt %)	0	10	20	30	100

Table 2: Chemical composition of coke and HDPE utilised in current study

Component	Moisture	Volatile Matter	Ash	Total Carbon	Fixed Carbon	Hydrogen	Sulphur	Nitrogen
Coke (wt %)	1.30	3.0	18.30	78.70	77.36	-	0.32	1.21
HDPE (wt %)	-	99.4	0.6	85.5	-	14.2	0.3	-

Table 3: Ash analysis of coke used in the study

Component	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	SO_3
Composition (wt %)	50.7	4.8	36.0	1.4	1.6	3.3	0.94	0.39	0.53	0.39

Table 4: Chemical composition (XRF) of iron ore (wt %)

Component	Fe_2O_3	SiO_2	Al_2O_3	CaO	MnO	ZnO	TiO_2	SO_3
Composition (wt %)	96.89	0.445	-	0.0225	0.020	0.0115	0.134	0.257

powder acted as a blank medium, since its reduction will be difficult at the selected temperature.

Reduction studies
A LECO™ crucible was selected as the sample container in a custom-made horizontal tube furnace (HTF) for the reduction studies (Fig. 1).

The electrically heated HTF tube has an inside diameter of 50 mm and was fabricated from double-walled, vacuum-insulated stainless steel tubes fitted with a cooling fan to dissipate heat. It is a micro scale reactor and is suitable for temperatures up to 1700 ℃.

The furnace tube was controlled by a digital mass flow meter throughout the experiment, while a high-resolution coloured charge-coupled device (CCD) camera provided with IRIS TV zoom lens was used to capture the live *in-situ* phenomena in the furnace. The melting of the composite pellet marked the beginning of contact time. The output from the camera was channelled to a TV monitor and a video cass-
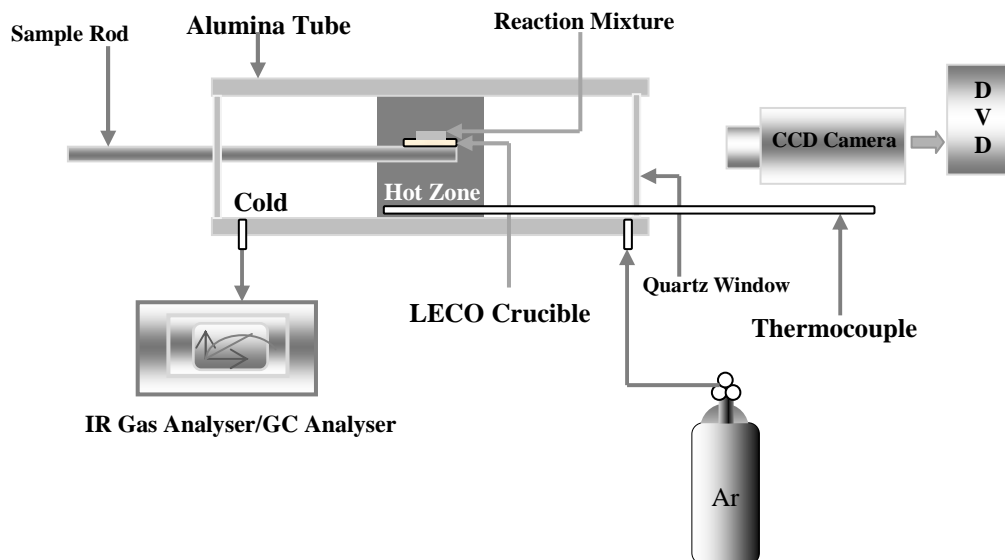
Fig. 1: Schematic representation of the horizontal furnace

ette recorder (VCR) to record the entire process as a function of time. An infrared gas analyser was attached to this system to monitor CH_4, CO and CO_2 gases produced by the reduction reaction and the results were recorded in a data-logging computer.

The sample assembly was placed in the furnace, which was purged continuously with argon (of 99.995% purity and flow rate 1L/min) to ensure inert conditions.

After the furnace had attained the desired hot zone temperature (1500°C), the sample was pushed into the reaction hot zone and gases were monitored for 1200s. This time was selected since initial trials showed no significant changes in gas composition or degree of reduction beyond 1200s.

Reacted carbonaceous material/iron oxide samples were quenched by rapidly withdrawing the tray from the reaction zone into the cold zone of the furnace. Particles of reduced iron metal,

which were clearly visible to the naked eye, were removed by a magnetic screw driver and its content was determined by the following chemical analysis methods:

- LECO™ C/S analysis for its C and S contents and

- LECO™ Oxygen analyser for its O content.

RESULTS AND DISCUSSION
Thermal decomposition behaviour of HDPE
The thermal decomposition behaviour of HDPE at 1500°C is illustrated in Figs 2 and 3. Two distinct features are noticeable from the thermal decomposition of HDPE:

- The generation of CH_4

- The generation of hydrogen, indicated by the sharp peak in Fig. 3.

Thus thermal decomposition of HDPE generates the gaseous reducing species CH_4 and H_2 into the reaction environment; this may enhance the overall reduction process.

NATURE OF REDUCED METAL
Nearly spherical samples of reduced metal were obtained for all blend proportions and the result for HDPE as the reducing agent is shown in
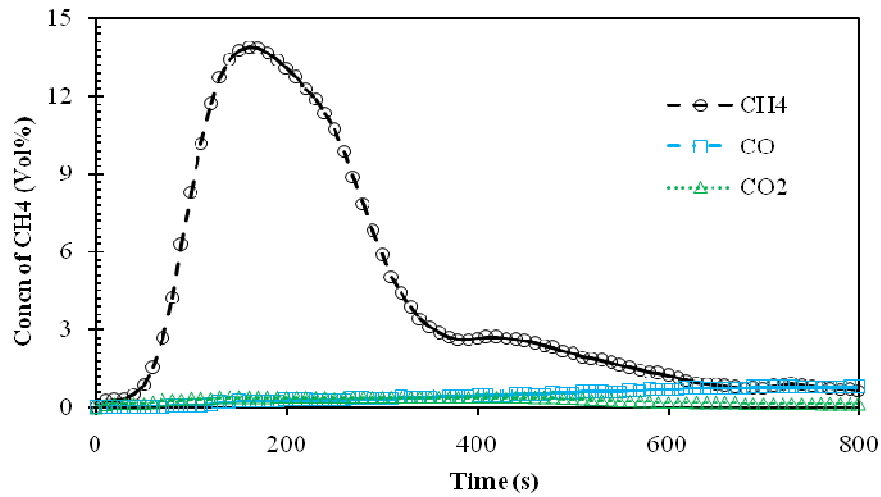

Fig. 2: Gas generation behaviour during the thermal decomposition of HDPE from a HDPE-alumina compact
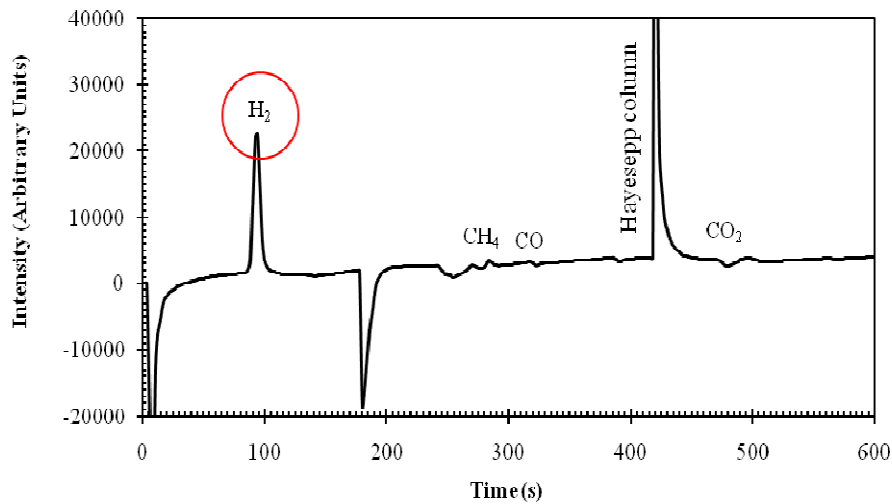

Fig. 3: Gas chromatogram obtained after 60s of heating HDPE-alumina compact

Fig. 4. The vigorous nature of the reaction is apparent from Fig. 4, where droplets of metallic iron are seen deposited across the entire volume of the crucible.

The conventional reductant for iron oxide reduction in industry is typically metallurgical coke and other forms of carbon, hydrogen and natural gas. Even without blending with any of the conventional reductants, this investigation has demonstrated that the heaps of waste plastics currently stockpiled on landfills or littered on the streets of various municipalities and metropolis could be diverted into the ironmaking industry as important chemical feedstock.

IR GAS ANALYSES

The contents of CO and CO_2 in the off-gas were measured continuously by an infrared (IR) gas analyser from which the rates of gas evolution ($\mu mol/s.g$-Fe) were calculated for each carbonaceous blend. The results are shown in Fig. 5. The rates of evolution of CO and CO_2 increased slowly for the first 200 seconds for HDPE (Fig. 5a), followed by a sharp rise, attaining maximum values of 154.4 and 16.6$\mu mol/s.g$-Fe after about 230s and 220s, respectively. Fig. 5b illustrates the gas generation behaviour of coke; active gas generation by coke commences almost immediately after pushing the tray into the hot zone and it attains maximum values of 108.8 and 30.0$\mu mol/s.g$-Fe after about 150s and 70s for CO and CO_2, respectively. CO_2 generation by coke is higher compared to HDPE, which has almost negligible CO_2 generation. Gas generation by HDPE-coke blends as in Figs. 5 (c-e) commenced earlier than HDPE but later than coke.

It is apparent from Fig. 5 that all the blends showed lower CO_2 evolution compared to coke and that CO_2 evolution generally decreased as the amount of HDPE blended with coke increased. For all the reductants, CO_2 and/or H_2O evolution are significantly lower than CO. The relatively lower values recorded for CO_2/H_2O compared to CO may be an indication of direct reduction of Fe_2O_3 by C or a dominant carbon gasification reaction by CO_2 (Boudouard reaction) and/or H_2O (oxidation of C by H_2O). These two reactions are highly endothermic and occur above 1000°C (Biswas, 1981), a tem-
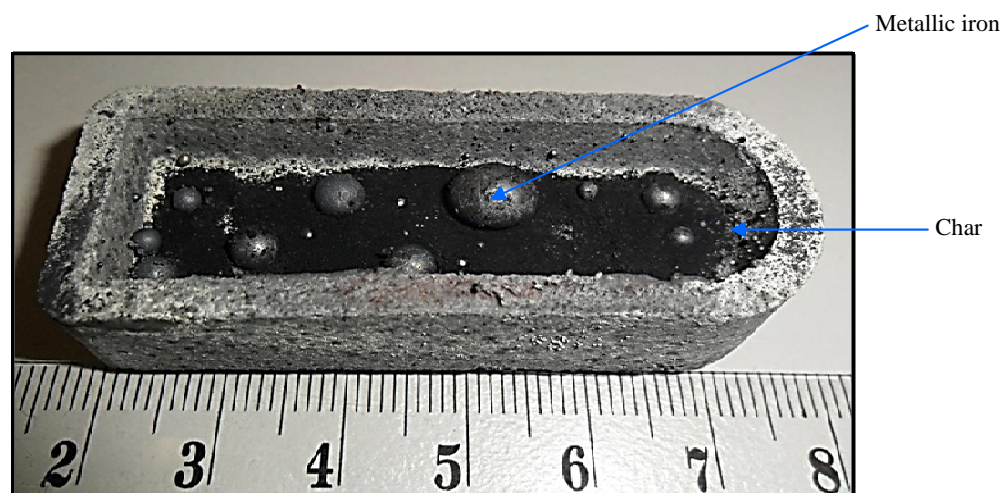

Fig. 4: Droplets of metallic iron and char obtained after reduction of red mud by HDPE (600s of reaction)

perature range that is within the experimental temperature of the current investigation. Another possible reaction is the direct reduction of Fe_2O_3 by CH_4, which was the predominant hydrocarbon gas detected in the off-gas in the initial stages of the reduction process.

$$3CH_4 + Fe_2O_3 = 2Fe + 6H_2 + 3CO \qquad (1)$$
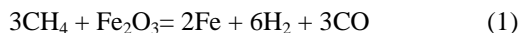
Fraction reacted as a function of time

The change in fraction reacted, *f,* was plotted as a function of time for coke, HDPE, and the blends (Fig. 6). In the first four minutes of reduction, no noticeable difference is observed

between the blends on one hand and coke on the other. However, reduction by coke slows down significantly after this period. A possible reason could be the high ash content (18.3wt %) of the coke utilised for this investigation; this could have coated the surface of the partially reduced metal and consequently inhibit further reaction.

From Fig. 6**,** the time for complete reduction of iron oxide was 600, 580, 330,330 and 340s for Coke, HDPE, Blend 1, Blend 2, and Blend 3, respectively, as the carbonaceous reductant. The times recorded in this investigation
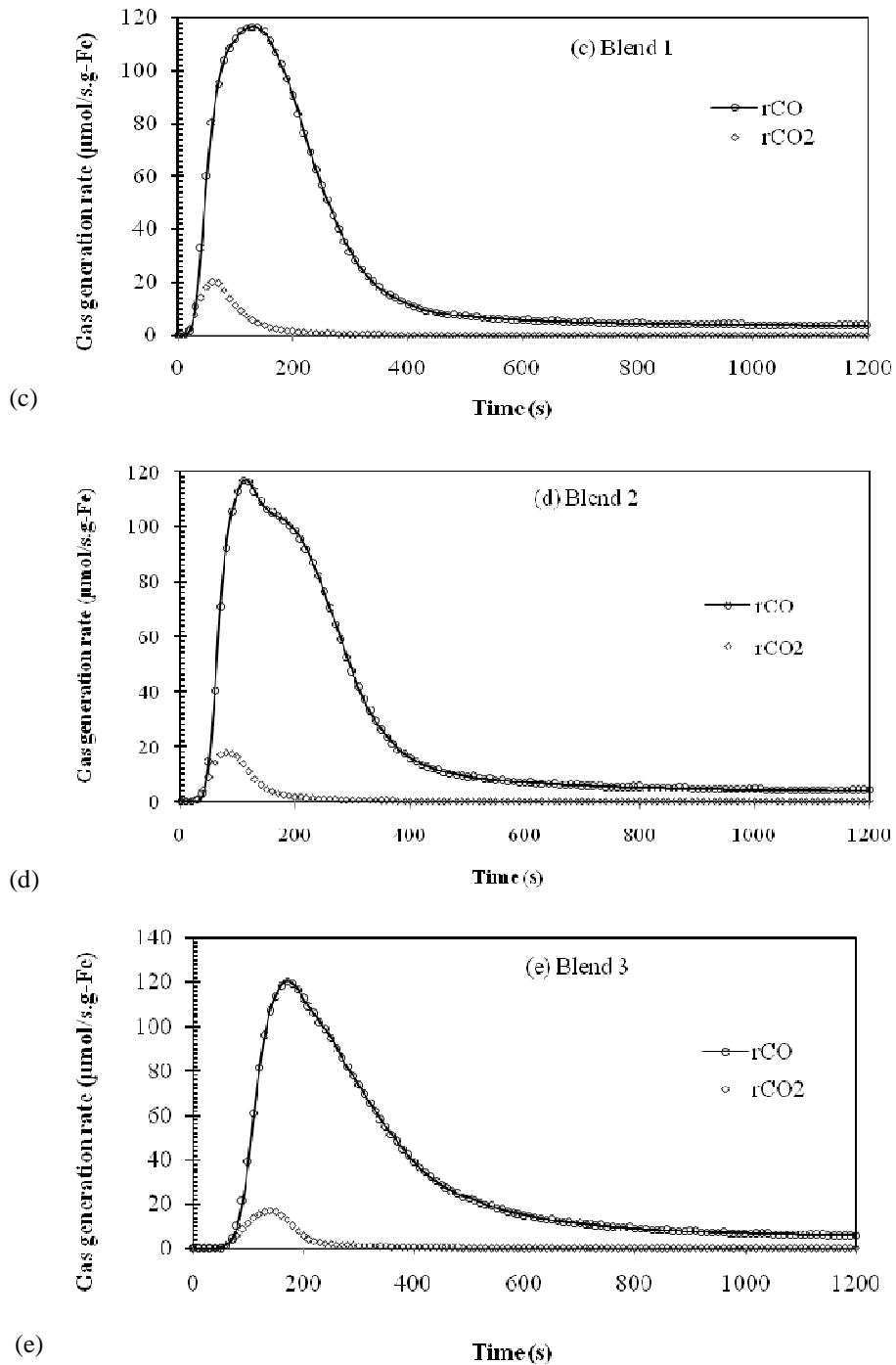

(a)

(b)

(c)

(d)

(e)
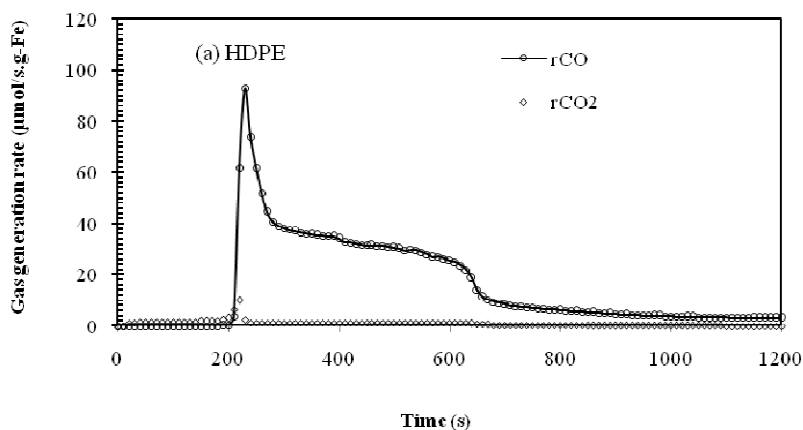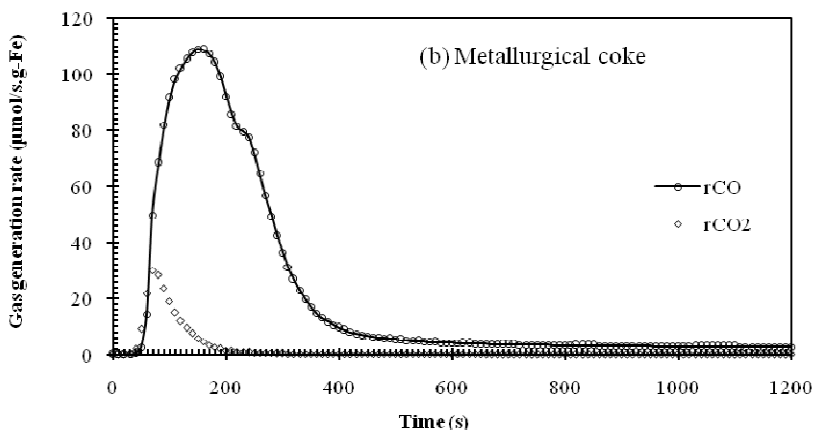
Fig. 5: Change in the rate of generation of CO and CO_2 with time for a) HDPE, b) Coke, c) Blend 1, d) Blend 2 and e) Blend 3
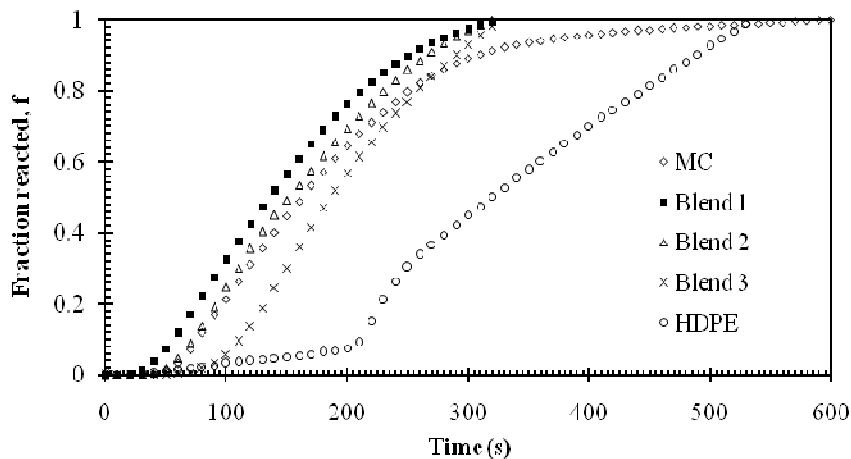
Fig. 6: Change in fraction reacted, *f*, with time for each carbonaceous reductant

agree with the observation by Kikuchi *et al.* (2010) that composite pellets of iron oxide-carbonaceous material could be reduced within 600s. Although HDPE has little or no fixed carbon, CH_4 generated in the initial stages of heating was converted to nascent carbon and hydrogen and the reaction was catalysed by freshly produced metallic iron, as observed by Murakami and Kasai (2011). Blending of coke with HDPE therefore promotes the generation of hydrogen in the reaction environment. Hydrogen gas, apart from being a faster reducing agent than both carbon monoxide and solid carbon (Sohn and Fruehan, 2005; Ono-Nakazato *et al.*, 2003), also enhances the rate of reduction of iron oxides by carbon monoxide (Ono-Nakazato *et al.*, 2003)when it is added to a reaction system containing the latter.

Peaks of hydrogen were detected in the off gas when the iron oxide was reduced by HDPE and the blends. No such peaks were visible when coke was used as the reductant (Fig.7)

As observed by Donskoi *et al.* (2003), CO_2 and H_2O produced from the reduction of iron oxide

gasify any available carbon at high temperatures to regenerate CO and H_2. Accordingly, a series of cyclic reactions is set up as CO and H_2 (products of the carbon gasification reactions) in turn partially react with any unreduced iron oxide and further reactions continue (Donskoi *et al.*, 2003; Shi *et al.*, 2008).These cyclic reactions persist until all the iron oxide has been reduced to metallic iron, provided there is enough carbon in the system (Shi *et al.*, 2008) as is the case in this investigation. It is thus clear that hydrogen along with some fixed carbon in a carbonaceous material is essential to initiate and maintain these cyclic reactions to obtain a high rate of reduction. This essential requirement is met when coke (77.36wt.% fixed carbon) is blended with HDPE (~ 14.2 wt. % H_2) and it explains why the blends generally-perform better than either coke alone or HDPE alone.

CONTENT OF CARBON IN THE RE-DUCED METAL
Carburisation of the reduced metal is required for lowering its melting temperature and obtaining a melt and slag separation at molten
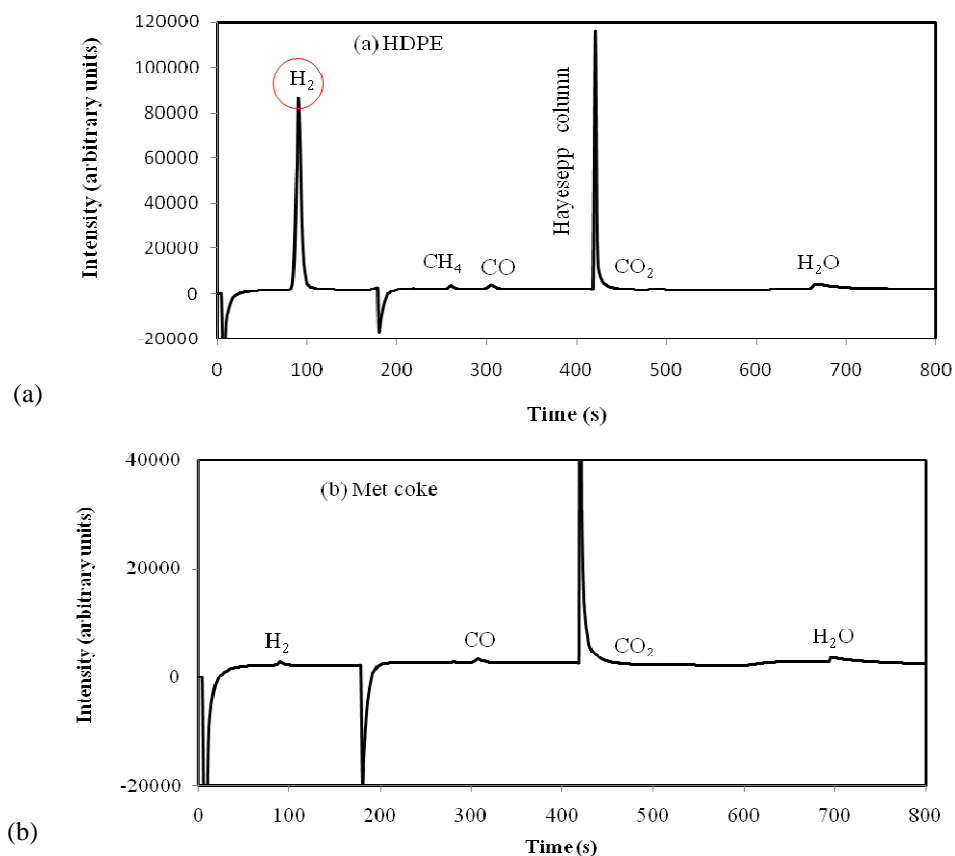
Fig. 7: Gas chromatogram obtained after reduction of iron oxide by (a) HDPE and (b) Coke for 60s at 1500°C

state. Besides, solute carbon has been documented to contribute to slag foaming if the reduced metal is subsequently used as iron feedstock for electric arc furnace steelmaking (Jones, 2007).
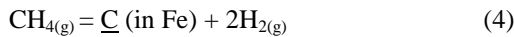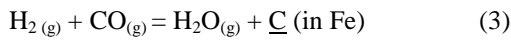
The content of carbon in the reduced metal was determined using a LECO Carbon/Sulphur analyser (model CS 230, LECO Corporation, Michigan, USA); the results are shown in Fig. 8. The highest level of carburisation was observed for Blend 3 (2.964wt%). Carburisation is lowest for HDPE(1.335wt %), followed by coke (1.643wt%), Blend 2 (1.880wt %) and

Blend 1 (1.943 wt %). Blending resulted in improved carburisation, as all the blends showed higher levels of carburisation than coke or HDPE. Dankwah *et al.*(2012) attributed increased levels of carburisation to the presence of a hydrogen environment along with the fixed carbon content of a carbonaceous reductant. In the absence of hydrogen the metal is carburised mainly by reaction 2. (Fruehan, 1973a; Fruehan 1973b):

$$2CO_{(g)} = CO_{2(g)} + \underline{C} \text{ (in Fe)} \qquad (2)$$

In a CO-H_2-CH_4 environment (due to thermal/ catalytic cracking and gasification of the

polymer) the reduced metal is carburised via three parallel reactions, which consist of reaction2 and the following (Fruehan, 1973a; Fruehan 1973b):

$$H_{2\,(g)} + CO_{(g)} = H_2O_{(g)} + \underline{C} \text{ (in Fe)} \qquad (3)$$

$$CH_{4(g)} = \underline{C} \text{ (in Fe)} + 2H_{2(g)} \qquad (4)$$

Fruehan (1973a) calculated an apparent rate constant for reaction3 that was over five times higher than that for reaction 2. Kaspersma and Shay (1980) determined the rate constant for carburisation by reaction3 to be sixteen times greater than that by reaction2 and twenty two times that by reaction 4. Karabelchtchikova (1997)calculated a rate constant for reaction 3 that was 30 and 100 times faster than reactions 2 and 4, respectively. It is apparent from the forgoing discussions that carburization through reaction4 is negligibly small and can be ignored. Additionally, in a hydrogen environment, carburisation through reaction2 is negligibly small, compared to that through reaction 3. While HDPE had no fixed carbon, coke had no hydrogen; the blends satisfy the condition for improved carburisation (hydrogen from the HDPE (14.2 wt %) and a relatively high level of fixed carbon from coke (77.36 wt %).

The metallic iron produced was spherical in each case (Fig. 4), indicating that it was formed from the liquid state. The experimental temperature of 1500 °C is below the melting point of iron (1536 °C); the near perfect spherical shape of the iron nuggets as observed in this investigation is only possible for higher carburisation or the presence of further alloying elements in the reduced metal. The level of carburisation achieved (including pure HDPE) is sufficiently high to justify the observation of near perfect spherical shape. Dankwah *et al.* (2012) observed that the time taken for complete melting of pellets decreased as the proportion of the polymer in the blend increased. No significant difference in the time for complete melting was observed in this investigation for the different blends used (melting time was 150 -250s). Accordingly, it can be concluded that the pellets were first reduced to form solid iron, followed by carburisation, melting and agglomeration of smaller particles into bigger lumps.
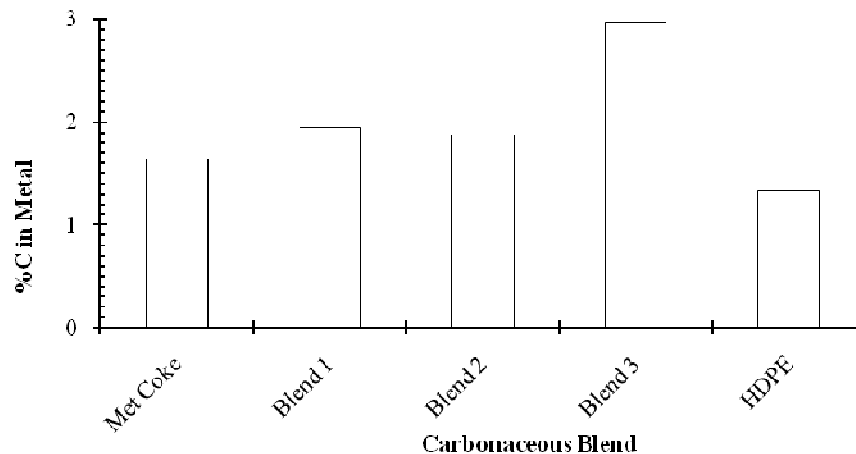

Fig. 8: Carburisation of the metal formed after reduction of iron oxide by each carbonaceous reductant at 1500 °C

Environmental considerations: Co_2 emissions The rate and relative amounts of CO_2 evolved after complete reduction of the iron oxide by each carbonaceous reductant replotted in Figs. 9 and 10, receptively. The reduction in CO_2 emissions over coke by the use of HDPE and each of the blends is plotted in Fig. 11. It is clear from Figs. 9 and 10 that the highest amount of CO_2 was produced from the reactions involving coke while the lowest value was recorded for HDPE. From Fig. 11, over 20% reduction in CO_2 emissions can be achieved by using HDPE or Blend 2 as a reductant instead of coke. The observed decrease in CO_2 emis-
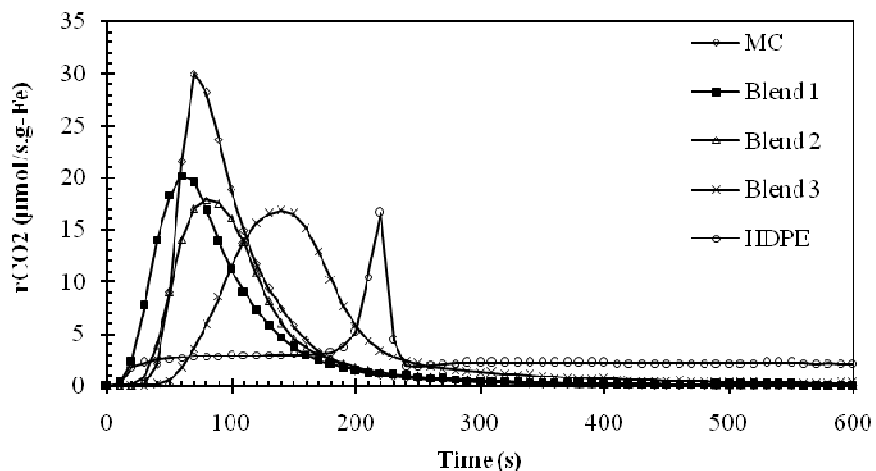
Fig. 9: Concentration of CO_2 generated by reactions of the hematite with each carbonaceous reductant
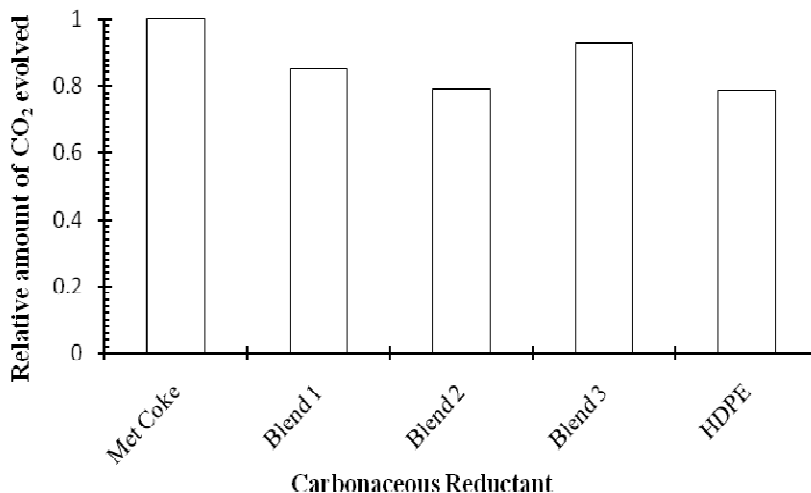
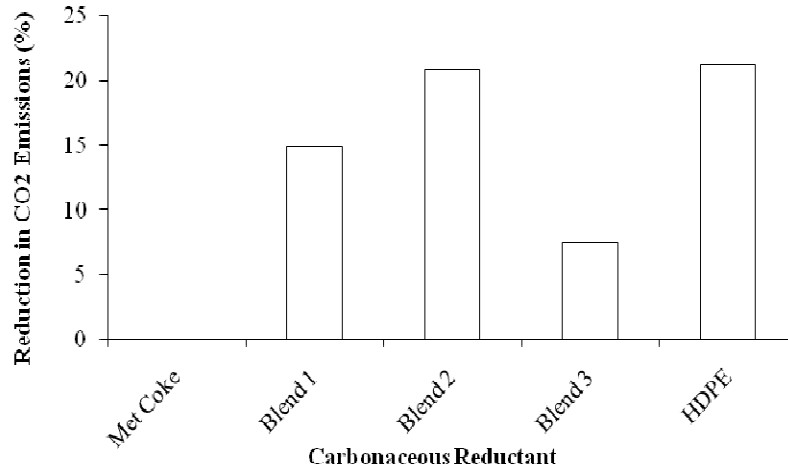**Fig. 10: Relative amounts of CO_2 generated after reduction**

Fig. 11: Reduction in CO$_2$ emissions over coke

sions with HDPE addition agrees with the observation by Matsuda *et al.* (2008) that it is possible to utilise waste plastics to produce metallic iron without generating CO$_2$. Singh *et al.* (2010) observed a 6.5% reduction in CO$_2$ emissions when coal was fired with 25% HDPE (measured in terms of thermal energy). They attributed this to the higher heating value of HDPE (46.2MJ/kg) as compared with that of coal.

CONCLUSIONS

A laboratory investigation has been conducted on the utilisation of HDPE and its blends with coke as reducing and carburising agents for the production of metallic iron from iron oxide.

The major findings of this investigation are:

(1) HDPE along with its blends with coke could be used effectively as reducing and carburising agents in iron oxide reduction.

(2) Blending of coke with HDPE resulted in:

• Significant improvements in the time re-

quired for complete reduction of iron oxide (from 600s for coke to 330s for blends 1 and 2).

• Improved carburisation of the reduced metal.

• Reduction in CO$_2$ emissions (over 20% decrease).

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